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ANALYSIS OF HEAVY METALS IN SLUDGE FROM INDUSTRIAL WASTEWATER TREATMENT PLANT

Reena Sabrina Binti Yusuf Latif

Bachelor of Science with Honours
(Resource Chemistry)
2006

ANALYSIS OF HEAVY METALS IN SLUDGE FROM INDUSTRIAL WASTEWATER TREATMENT PLANT

REENA SABRINA BINTI YUSUF LATIF

This project is submitted in partial fulfillment of the requirements for the degree of Bachelor of Science with Honours (Resource Chemistry)

Faculty of Resource Science and Technology
UNIVERSITI MALAYSIA SARAWAK

2006

DECLARATION

No portion of the work referred to in this dissertation has been submitted in supports of an application for another degree of qualification of this any other university or institution of higher learning.

(REENA SABRINA BT YUSUF LATIF)

Programme of Resource Chemistry

Faculty of Resource Science and Technology

Universiti Malaysia Sarawak

ACKNOWLEDGEMENT

First and foremost, I would like to thank Miss Devagi Kanakaraju for her constant support, encouragement assistance and ideas throughout the process of completing my research. Thanks are also due to all lab assistants of FRST. Their help and guidance is very crucial in making my research successfully.

I would also like to extend my gratitude to my parents for their support and understanding in making this research as successful one. Last but not least, I am also grateful for the cooperation and generosity shown by my fellow friends while doing this research.

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ANALYSIS OF HEAVY METALS IN SLUDGE FROM INDUSTRIAL WASTEWATER TREATMENT PLANT

Reena Sabrina Binti Yusuf Latif

Faculty of Resource Science and Technology
Chemistry Resource Programme
Universiti Malaysia Sarawak

ABSTRACT

The presence of heavy metals in the sludge produced in wastewater treatment plant restricts plants growth hence their use for agricultural purposes. Studies have shown that the sludge is suitable for land application since it rich in nutrients. The aim of this study was determine the levels of potential toxic elements namely Fe, Cu, Mn, Cr, Pb and Zn in the raw sludge samples from industrial wastewater treatment plants of Tex Cycle by employing Flame Atomic Absorption Spectroscopy (FAAS). In addition, the sludge samples also have been characterized for pH, organic matter and particle size distributions and also analyzed for their nutrient contents (N and P). The highest element present in the sludge samples was Fe and the least abundant element was Mn. The levels of heavy metals content in the sludge did not exceed the limits designated by Environmental Protection Agency United State and European Legislation. The sludge is suitable to be applied as soil amendment and also can be used as fertilizers since it has high organic matter content and rich in nutrients (N and P).

Key words: sludge; wastewater treatment plant; heavy metals; nutrients

ABSTRAK

Kehadiran logam berat dalam enap cemar yang dihasilkan dari loji rawatan sisa kumbahan boleh menyekat pertumbuhan tumbuh-tumbuhan apabila enap cemar digunakan untuk tujuan pertanian. Kajian lepas telah menunjukkan bahawa enap cemar ini sesuai digunakan untuk tujuan pertanian kerana ia kaya dengan nutrien. Objektif kajian ini adalah untuk menentukan kepekatan logam berat seperti Fe, Cu, Mn, Cr, Pb dan Zn yang terkandung di dalam enap cemar dari loji rawatan sisa kumbahan industri TexCycle dengan menggunakan Spektroskopi Serapan Atom Nyala. Nilai pH, bahan organik, saiz zarah, dan kandungan nutrien iaitu nitrogen dan fosforus yang terkandung di dalam enap cemar tersebut dianalisis komposisinya. Fe mempunyai kepekatan ynag tertinggi manakala Mn mempunyai kepekatan yang terendah di dalam enap cemar yang telah dikaji. Kepekatan logam berat yang terkandung di dalam enap cemar didapati berada di bawah had yang telah ditetapkan oleh "Environmental Protection Agency United State" dan "European legislation". Enap cemar yang telah dianalisis didapati sesuai digunakan sebagai "soil amendment" dan sebagai baja kerana ia mempunyai kandungan bahan organik yang tinggi dan kaya dengan nutrien seperti nitrogen dan fosforus.

Kata kunci : enap cemar; loji rawatan sisa; logam berat; nutrien

CHAPTER ONE

INTRODUCTION

1 RESEARCH BACKGROUND

The accumulation and production of sewage sludge from urban wastewater treatment ants is a growing environmental problem due to the demand of better water quality (Fuentes *al.*, 2004; Wong *et al.*, 2001). Malaysia generates more than 3 million tonne of domestic ewage sludge per year and the figure is rising in proportion to the population increase (Idris, 005). In New York State, approximately 370,000 dry tonne of sludge per year, or about ,000 dry tonne per day, are produced. New York City alone generates about 400 dry tonne of ludge everyday (Cleland *et al.*, 1996).

Landfilling and incineration are identified as potential options for the disposal of ewage sludge. Disposal of sewage sludge by landfilling is a feasible option currently racticed in many parts of the world. However, the scarcity of land makes landfilling costly nd inappropriate in the long term (Wong *et al.*, 1999). In addition, the high rainfall results in high volume of leachate generation, which represents a potential source of contamination of round water, water courses, or water bodies (Kelley, 1981; Chaney, 1983; Li and Corey, 993). Incineration can effectively reduce the volume of waste and sterilize the end product. Iowever, incineration requires a high capital and operation cost. It also needs intensive nergy demands (Girovich, 1996). The possibility of generation of odour and air pollutants nd the disposal of toxic ash generated would also cause a potential environmental hazard Girovich, 1996; Lei *et al.*, 2000). Both of these disposal strategies will cause potential environmental problems that effect the health and living environment of human beings. Furthermore, the resource in the sludge can never be reused again (Wong *et al.*, 2001).

Recycling of waste for agricultural use is a useful alternative to incineration since they can act as a source of nutrients for crops due to their high organic matter content (Smith, 1996). Applying sludge to croplands or land application is a solution to the dilemma of accumulating sludge and also as another attractive option for sludge treatment and disposal (Chereminisinoff, 1994). These ways are not only to treat the waste but also to reutilize the residual resource in the sludge for the waste authority (Wong and Su, 1997). Sludge as fertilizers or as organic soil regenerators seems to be an attractive possibility because it would enable valuable components such as organic matter, nitrogen (N), phophorus (P) and other nutrients necessary for plant growth to be recycled (Hernandez *et al.*, 1991; Smith, 1996; Zufiaurre *et al.*, 1998). Sludge has a large amount of organic matter that can improve soil physical properties such as soil aeration and water holding capacity (Guidi *et al.*, 1990; Logan and Harrison, 1995). However, this practice represents a potential threat to the environment due to the possible high heavy metal contents, a problem that may be aggravated if the toxic metals are mobilized in the soil which will eventually be taken up by plants or transported into drainage waters (Angelidis and Gibbs, 1991; Mingot *et al.*, 1995; Alonso *et al.*, 2002).

.2 OBJECTIVES

With the exponential increase in waste sludge resulting from the public demand for wastewater treatment, the deposition of these sludges has increased over the past twenty years (Paul, 1994). Finding a safe place to dispose and put the sludge use it has proven troublesome and the problem is aggregated by the mushrooming numbers of water treatment plants in this country. Improper understanding and disposal of wastes continues to be a hot issue among environmentalist, public and also government. Hence, it is crucial to monitor the concentrations of heavy metals to prevent addition of excess amounts of metals released to groundwater/land and eventually to the aquatic ecosystem.

Sludge contains many nutrients needed for plant growth including nitrogen and phosphorus. Whether the sludge from treatment plant should be used as fertilizers or not also depends on their heavy metal content (Fuentas *et al.*, 2004). Hence, the analysis of heavy metals, nutrients and other parameters from the sludge have been carried out in order to examine whether the sludge from Tex Cycle are suitable to be applied as soil amendment and fertilizers.

The study was done in order to determine the concentrations of potential toxic elements namely Iron (Fe), Copper (Cu), Nickel (Ni), Manganese (Mn), Chromium (Cr), Lead (Pb) and Zinc (Zn) in the raw sludge samples. The raw sludge samples also have been characterized for pH, organic matter (OM) and particle size distributions, and also analyzed for their nutrient contents namely Total Kjedahl Nitrogen (TKN) and Total Phosporus (TP).

CHAPTER TWO

LITERATURE REVIEW

2.1 SLUDGE

According to Cheremisinoff (1994), sludge is a generic term for solids separated from suspension in a liquid by a variety of processes. It is an end product of the wastewater treatment process. It is the solid material remaining after sewage treatment facilities purifies wastewater from residential, commercial, agricultural and industrial areas. In some communities, runoff from roads, lawns and fields is also sent through the facility (Cogger and Sullivan, 1991).

Sludge is typically produced by physical separation and by the biological and chemical treatment of wastewater (Cheremisinoff, 1994). Sources of sludge include sewage treatment plant and industrial wastewater treatment facilities. Different wastewater treatment systems produce sludge in different ways and amounts (EPA, 1992). Sludge intended for land application typically looks like wet peat moss or liquid manure and has a slight earthy scent (Muse *et al.*, 1991). To determine whether biosolids or municipal sewage sludge is suitable for organic production the entire process of wastewater treatment and sludge production must be considered (Bevacqua and Mellano, 1993)

Treatment of municipal wastewater produces different types and volumes of sludge (Cleland *et al.*, 1996). Raw primary sludge is produced during the first phase of wastewater treatment. Primary treatment removes 40-50% of the solids in the water. They are removed by bar screens, grit chambers and primary sedimentation tanks. Primary sludge contains solid organic material. Secondary sludge is generated after the wastewater travels through an aeration tank. It consists of microscopic material which remains after biological processes have removed dissolved organic matter. The third stage of water treatment generates tertiary sludge by advanced processes such as chemical treatment and filtration (Chaney and Ryan, 1991).

Land application is a natural way of recycling sludge. However, there are problems associated with land application of sludge, including odours and aesthetics, potential pathogens in sludge, suitable site and soil, and sludge quality with respect to toxic organic chemicals, salts, and heavy metals (Robert and Winkler, 1991; Wong, 1995; Krebs *et al.*, 1998). Besides that, this application is limited by the level of several contaminants, such as toxic heavy metals, which may enter into the human food chain through the consumption of cultivated plants or contaminated waters, causing risks for human health (Smith, 1996).

2.2 WASTEWATER TEATMENT

Industrial wastewater treatment covers the mechanisms and processes used to treat waters that have been contaminated in some way by man's industrial or commercial activities prior to its release into the environment or its reuse (Dunn and Julie, 1997). Wastewater treatment is the process of removal the objectionable items, nutrients and heavy metals. They were produce two products. There are clean water and sludges. The clean water was retuned to streams while the sludges must be landfilled, incinerated or recycled as a soil amendment (Muse *et al.*, 1991).

Wastewater treatment process commonly involves 3 steps. There are preliminary eatment, primary treatment and secondary treatment (Figure 1.0) (Muse *et al.*, 1991).

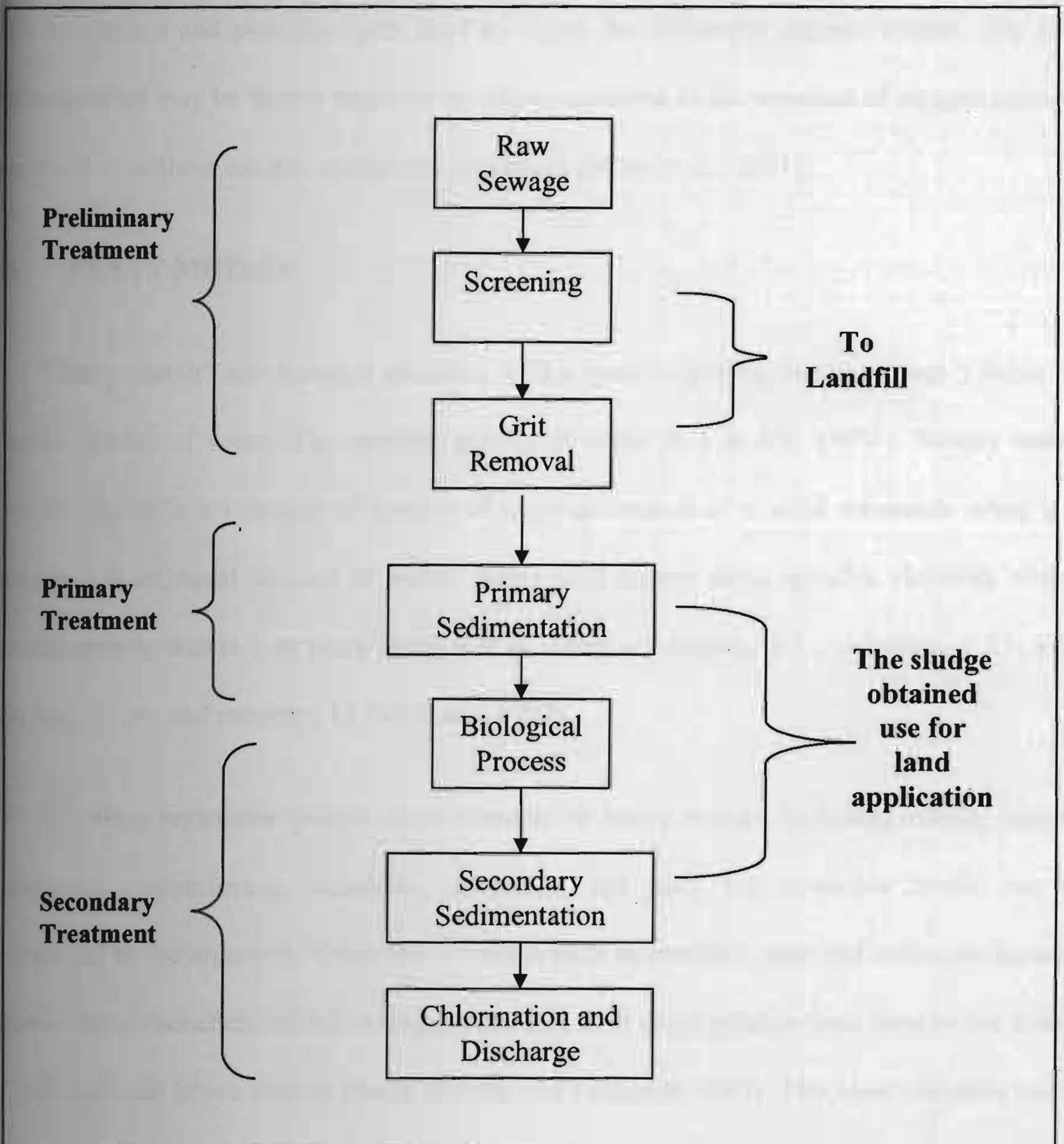

Figure 1.0: The process of wastewater treatment plant

Preliminary treatment involves screening and grit removal treatments. Screening is the rocess to remove large floating object such as sticks, paper and rags while grit removal is to etain inorganic solid such as grit, sand and cinders. All of this material is usually landfilled and does not contribute to sludge (Muse *et al.*, 1991; Cheremisinoff, 1994). Secondary or biological treatment is step to remove biological oxygen demand (BOD). Microorganisms such as bacteria and protozoa were used to digest the remaining organic matter. The final sludge product may be further digested by microorganisms in the presence of oxygen (aerobic digestion) or without oxygen (anaerobic digestion) (Muse *et al.*, 1991).

2.3 HEAVY METALS

"Heavy metals" are chemical elements with a specific gravity that is at least 5 times the specific gravity of water. The specific gravity of water is 1 at 4°C (39°F). Simply stated, specific gravity is a measure of density of a given amount of a solid substance when it is compared to an equal amount of water. Some well-known toxic metallic elements with a specific gravity that is 5 or more times that of water are arsenic, 5.7 ; cadmium, 8.65; iron, 7.9; lead, 11.34; and mercury, 13.546 (Lide, 1992).

Living organisms require trace amounts of heavy metals, including cobalt, copper, manganese, molybdenum, vanadium, strontium, and zinc, but excessive levels can be detrimental to the organism. Other heavy metals such as mercury, lead and cadmium have no known vital or beneficial effect on organisms, and their accumulation over time in the bodies of mammals can cause serious illness (Raven and Loeppert, 1997). The most common heavy metals implicated in acute and/or chronic conditions include lead, arsenic, and mercury (David and Ferner, 2005). Heavy metal toxicity is frequently the result of long term, low-level exposure to pollutants common in our environment: air, water, food, and numerous consumer products. Exposure to heavy metals has been linked with developmental retardation, cancer, kidney damage and even death (David and Ferner, 2005).

2.3.1 Heavy Metals in Sludge

The amounts of heavy metals in sludge vary from source to source, based on the treatment process, origin, types and quantities of wastewaters treated (Muse *et al.*, 1991; Wong and Su, 1997). Besides that, the sludge also contains nutrients which are helps to improve the soil structure and workability of most soils. Organic matter also improves water retention, permits easier root penetration and reduces water runoff and soil erosion (Guidi *et al.*, 1990; Logan and Harrison, 1995).

Preventing heavy metal pollution is critical because cleaning contaminated soils is extremely expensive and difficult. Applicators of industrial waste or sludge must abide by the regulatory limits set by the U.S. Environmental Protection Agency (EPA) Part 257, 403, 503 in Table 2.1, the regulatory limits on heavy metals applied to sewage sludge adapted from Canadian normalization (CCME) in Table 2.2 and the limits established by European legislation (Directive 86/278/EEC) in Table 2.3.

Table 2.1: The Regulatory limits on heavy metals applied to soils

Elements	Maximum concentration in sludge in (mg/kg)
Arsenic	75
Cadmium	85
Chromium	3000
Copper	4300
Lead	420
Mercury	840
Molybdenum	57
Nickel	75
Selenium	100
Zinc	7500

*** Adapted fromU.S. EPA, Part 257, 403, 503, 1993**

Table 2.2: The Regulatory limits on heavy metals applied to Sewage Sludge

Elements	Limit values Class A "which have no restrictions in use" (mg/kg)	Limit values Class B "which can be used on forest lands and road sides and for other landscaping purposes" (mg/kg)
Zn	500	1850
Cu	100	757
Pb	150	500
Ni	62	180
Cd	3	20

***Adapted from Canadian normalization CCME, 1995**

Table 2.3: The Regulatory limits on heavy metals applied to Sewage Sludge destined for agricultural use

Elements	Threshold value (mg/kg)
Cd	20-40
Cu	1000-1750
Ni	300-400
Pb	750-1200
Zn	2500-4000
Cr*	1000-1500

* Values stipulated by Spanish law

Many studies have been carried out on the speciation of heavy metals in sludge and soils amended with composted sewage sludge or raw sludge (Tessier *et al.*, 1979; Sposito *et al.*, 1982; Sims and Sklin, 1991; Pichtel and Anderson, 1997). Petruzzelli *et al.* (1994) suggested that the speciation of each metal in the sewage sludge compost depends on its initial chemical state in the sewage, the adsorption and precipitation mechanisms in sludge, and the effect of stabilization of the material and the humification process that occurs during composting on the chemical form of the metal.

The treatment by composting leads to the development of microbial populations, which cause numerous physico-chemical changes within mixture. These changes could influence the metal distribution through release of heavy metals during organic matter mineralization or the metal solubilization by the decrease of pH, metal biosorption by the microbial biomass or metal complexation with the newly formed humic substances or other factors (Brauckman, 1990; Hsu and Lo, 2001; Zorpas *et al.*, 2003). Hsu and Lo (2001) reported the increase of metal concentrations during composting of swine manure and suggested that the types of composting and raw materials are of major importance to metal condensation.

Research done by Nathalie *et al* (2002), reported that composting the sludge in 30 days can decrease the levels of heavy metals that content in sludge while after composting the sludge within 60 days the levels of heavy metals increase in small amount and after 90 days the levels of heavy metals in sludge decrease again. Neither total nor available heavy metal concentrations were increased in the soil by sewage sludge compost application. Indeed, the composting process reduces the heavy metal availability in the raw material, possibly due to adsorption on or complexing by humic substances (Pare *et al.*, 1999; Shuman, 1998; Pichtel and Anderson, 1997). From the study they obtained that the levels of the heavy metals in sludge sample before composting were Cu, 36.0 mg/kg; Zn, 285.0 mg/kg; Ni, 26.0 mg/kg and Pb, 14.5 mg/kg and after the composting of 30 days, the levels of heavy metals were decreased to Cu, 35.0 mg/kg; Zn, 252.7 mg/kg; Ni, 24.7 mg/kg and Pb, 13.0 mg/kg. After 60 days of composting the levels of heavy metals increase only in small amount which were Cu, 36.1 mg/kg; Zn, 252.9 mg/kg; Ni, 25.7 mg/kg and Pb, 14.0 mg/kg. The levels of heavy metals after 60 days composting still lower than the sludge before composting while after 90 days of composting, levels of heavy metal in sludge were decrease to Cu, 34.0 mg/kg; Zn, 250.7 mg/kg; Ni, 23.7 mg/kg and Pb, 11.0 mg/kg. Small amounts of heavy metals presence in the sludge after have been composting make it suitable to apply as fertilizers.

According to the study done by Amir *et al.*, (2004), the main physico-chemical properties of the raw sludge such as pH, organic matter (OM), total kjedahl nitrogen (TKN), P total, Ca total, Mg total, Na total, K total, Mn total and Fe total were based on source of the raw sludge itself. The physico-chemical properties also depends on its initial chemical state in the sewage, the adsorption and precipitation mechanisms in sludge, and the effect of stabilization of the material and the humification process that occurs during storing on the chemical form of the metal. Sewage sludge samples which were taken from an anaerobic lagoon in this experimental wastewater treatment plant of Marrakech city (Morocco), was showed pH values ranged between 6 to 7.5. The value of the OM and TKN were 31.3 % and 1.3 % respectively. Total P, Ca, K, Mg, Na as well as Fe and Mn were more important to use this material as mineral fertilizers. Total concentration of metals (Zn, Pb, Cu, Ni, Cd) in the raw sludge was in the order of Zn > Pb > Cu > Ni > Cd. The values of the heavy metal contents in the sludge were Zn, 275 mg/kg; Cu, 71 mg/kg; Pb, 135 mg/kg; Ni, 24 mg/kg.

Fuentes *et al* (2004) reported that either the sewage sludges from treatment plants should be used as fertilizers or not depend on their heavy metal content. Sludge samples were collected from urban wastewater treatment plants located in the Region of Murcia SE Spain. From the study, they found that the total of heavy metal content of the sludge was Cu, 167 mg/kg ; Cr, 71mg/kg ; Ni, 15 mg/kg ; Fe, 8915 mg/kg ; Zn, 697 mg/kg ; Pb, 250 mg/kg ; and Cd, 11.4 mg/kg. The pH value of sewage sludges varies from 6.0 to 8.2 and the phosphorus content depends to a large extent on the stabilization process used. The value of OM, total N and total P are 26.3 %, 1.63 % and 0.42 % respectively. This study concluded that the sludge analysed was suitable for soil amendment since it has high organic matter content and rich in nutrients (N and P). Heavy metals in the sludge were below the limits laid designated by European legislation.

According to the Perez-Cid *et a*l., 1998, the determination of heavy metals in sewage sludge has received an increasing attention, since its agricultural use as fertilizers requires strict information about the metal composition of the sample. The sewage sludge sample that used in this study was collected from an urban wastewater treatment plant which is located in Ourense town (Spain). From the study, they obtained that the total heavy metal contents in a sludge sample was Cu, 428.6 mg/kg; Cr, 15.3 mg/kg ; Ni, 26.8 mg/kg ; Pb, 242.0 mg/kg and Zn, 694.8 mg/kg. The total metal content in the sludge was determined using the microwave digestion procedure.

CHAPTER THREE

MATERIALS AND METHODS

3.1 SAMPLE COLLECTION

The sludge samples were provided by wastewater treatment plant of Tex Cycle Sdn. Bhd. which is located in Selangor. Samples were collected in the months of August, October and December, 2005.

Tex Cycle is a recycling company that deals with toxic hazardous waste or more commonly known as schedule waste. The waste originates from various sources such as printing companies, automotive industries, chemical industries, oil industries and other manufacturing companies.

From year to year, the quantity of sludge produced by Tex Cycle's treatment plant is increasing. The sludge was disposed by landfilling and incineration. Both of these methods are expensive and also could lead to pollution. With the increases of the sludge every year, application the sludge as agricultural use might be the best solution. Stabilized sludge has been used for decades as a valuable soil additive (Muse *et al.*, 1991).